

## The effect of introduced method of titania and applied potential on the photoelectrocatalytic properties of CNT/TiO<sub>2</sub> electrodes

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**Abstract** In this paper, three types of CNT/TiO<sub>2</sub> composite electrodes were prepared with different methods. The changes in XRD patterns showed that the Electrode A contained a mixed phase of anatase and rutile while the Electrode B and Electrode C contained a typical single and clear anatase crystal structure. From SEM micrographs, TiO<sub>2</sub> particles were adhered on the surface of the CNT network in the forms of small clusters. The results of chemical elemental analysis indicated that the main elements such as C, O and Ti were existed. The results demonstrated that the efficiency of photoelectrocatalytic (PEC) oxidation for methylene blue (MB) was higher than that of photocatalytic (PC) oxidation. There was a clear enhancement trend of the MB degradation using the prepared CNT/TiO<sub>2</sub> composite electrodes with an increase of applied potential. Finally, the prominent PEC activities of the CNT/TiO<sub>2</sub> composites could be attributed to combination effects of photo-degradation of TiO<sub>2</sub>, electron assistant of CNT and function of applied potential.

**Key words** CNT/TiO<sub>2</sub> Electrode, Potential, Photoelectrocatalytic, Methylene blue

### 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) has always been one of the best candidate materials due to its photocatalytic properties, its relative nontoxicity, and long-term thermodynamic stability. Recently the hot field is how to enhance the photocatalytic properties [1]. Carbon nanotubes (CNT) have excellent mechanical properties and a large specific surface area ( $> 150 \text{ m}^2 \text{ g}^{-1}$ ) [2, 3], which are also allowed for surface chemical modifications to control the type of bonds that can be formed with titania, be it chemically bonded or van der Waals bonded. The mixture of titania and CNT also has a large area where pollutants (organic or inorganic reactants) can adsorb. Adsorption is a key process in the photocatalytic destruction of pollutants, as will be discussed later. Thus, CNTs are good dopants and supports for titanium dioxide samples to be used as photocatalysts.

CNT/TiO<sub>2</sub> composites are expected to be developed as a robust means to address various environmental and self-cleaning issues. Up to now, several groups managed to enhance their photocatalytic properties and optimized titania's use to degrade various organic and inorganic pollutants in several ways such as sol-gel [4-

13], hydrothermal [14] and electrospinning [15]. An et al. [4] deposited anatase TiO<sub>2</sub> onto CNTs via hydrolysis of titanium isopropoxide in supercritical ethanol and studied the photocatalytic activity of these composites in terms of their ability to mediate the degradation of phenol under visible light. Wang et al. [5, 6] used a modified sol-gel method to prepare CNT-TiO<sub>2</sub> composites that exhibited photocatalytic activity under both UV and visible light. Jitianu et al. [7] coated CNTs with anatase by using a sol-gel method and titanium alkoxides as precursors. Recently, CNTs have also been coated via hydrothermal methods [14]. A relatively new method of preparing such composites is the filter-mat or fiber-form via the electrospinning method [15].

However, the conventional preparation techniques usually suffer from their inherent disadvantages. Two problems that need to be addressed with high cost and time consuming for the particle-fluid separation after radiation treatment and the reuse of the catalyst restrained its industrial applications. So supported structures are needed. One approach is possible: embedding them into a matrix. In additional, applying a bias larger than the flat band potential of a semiconductor electrode can enhance the separation of photogenerated charge carriers, with the electrons moving toward the bulk of the crystal and the holes migrating toward the surface, under the influence of the electric field across the depletion layer [16-20]. Electrons and holes generated beyond the depletion

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layer also diffuse, and become separated, as a result of the electric field. Therefore, the quantum efficiency is increased with the benefit of no particle needing to be separated from the suspension system after the reaction because semiconductor films are immobilized on the substrate. To date, however, little attention has been paid to photoelectrocatalytic (PEC) systems employing CNT/TiO<sub>2</sub> composites as photoanodes. Therefore, it is necessary to explore simple and effective ways to synthesize CNT/TiO<sub>2</sub> composite electrode.

In this study, we prepared three types of CNT/TiO<sub>2</sub> electrodes to examine their PEC activity. The prepared electrodes were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX). The catalytic efficiency of the prepared electrodes was evaluated by the PEC degradation of an azo compound, methylene blue (MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl<sub>3</sub>H<sub>2</sub>O).

## 2. Experimental

### 2.1. Materials

Carbon nanotubes (CNTs) were selected as the support material. The CNTs (Multiwall nanotubes, diameter: ~20 nm, length: ~5 μm) supplied from Carbon Nano-material Technology Co., Ltd, Korea, were used without further purification. The pristine TiO<sub>2</sub> was commercially available and was supplied from Duksan Pure Chemical Co., Ltd, Korea. The titanium n-butoxide (TNB, Ti(OC<sub>4</sub>H<sub>7</sub>)<sub>4</sub>) as a titanium source for the preparation of CNT/TiO<sub>2</sub> composites were purchased from Acros Organics, New jersey, USA. For the oxidation the surface of CNT, *m*-chloroperbenzoic acid (MCPBA) was used as an oxidized reagent which was purchased from Acros Organics, New Jersey, USA. The novolac typed phenol resin (PR) was supplied from Kangnam Chemical Co., Ltd, Korea. Benzene (99.5 %) was used

as an organic solvent which was purchased from Samchun Pure Chemical Co., Ltd, Korea. The MB was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, Korea. It was selected because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines.

### 2.2. Preparation of CNT/TiO<sub>2</sub> electrodes

Several CNT/TiO<sub>2</sub> electrodes were prepared. The preparation procedures for the electrodes were given in Fig. 1. A mixture of CNT, TiO<sub>2</sub> and PR powders in a CNT : TiO<sub>2</sub> : PR weight ratio of 6 : 4 : 1 was moulded under the pressure of 250 kg/cm<sup>2</sup> and heat treated at 673 K for 1 h, the dimension of CNT/TiO<sub>2</sub> electrodes was 9.95 mm × 39.5 mm × 5.95 mm (Electrode A).

Electrode B was obtained as the following procedure: for preparing the oxidizing agent, 2.0 g MCPBA was melted in 60 mL benzene. And then 0.6 g CNT was put into the oxidizing agent, refluxed for 6 h, filter and dry. The oxidized CNT was put into the mixing solution of TNB and benzene with different ratios of volume. Then the solutions were homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After the stirring the solutions were transformed to the CNT/TiO<sub>2</sub> gels, and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. And then 0.4 g PR was added into these CNT/TiO<sub>2</sub> composites, the composites were pressed at the pressure of 250 kg/cm<sup>2</sup> in a mould, which the dimension was 9.95 mm × 39.5 mm × 5.95 mm. And then heat treated at 673 K for 1 h, the CNT/TiO<sub>2</sub> electrodes were prepared.

For the preparation of Electrode C, 0.4 g PR was mixed with 0.6 g CNT, and then the CNT matrix electrodes were pressed at the pressure of 250 kg/cm<sup>2</sup> in a mould. The dimension of CNT matrix electrodes was 9.95 mm × 39.5 mm × 5.95 mm. The curing temperature of the CNT matrix electrodes was 423 K, and the cured sample pyrolyzed at 673 K for 1 h in order to com-

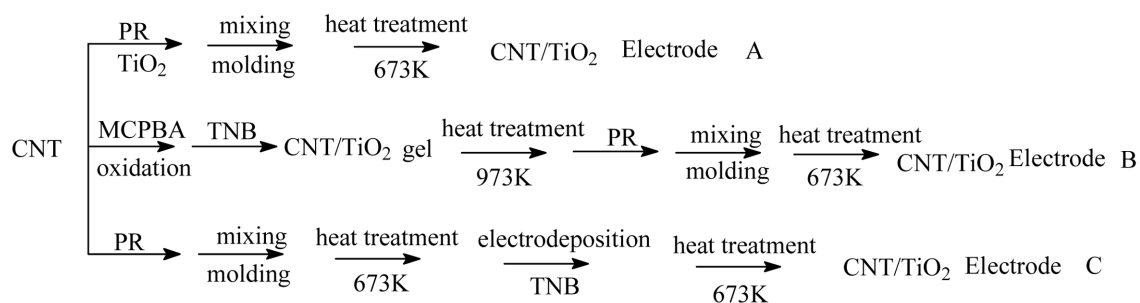


Fig. 1. Fabrication process of CNT/TiO<sub>2</sub> electrodes.

pletely cure the binder. Then the mixing solution of TNB and benzene with volume ratio of 1 : 1 was used as an electrolyte. The counter electrode of the same size was artificial graphite (TCK, Korea). The applied voltage of the preparation of CNT/TiO<sub>2</sub> composites was set to 9.0 V with 10 minutes. Before heat treatment, the solvent in the matrix was vaporized at 343 K for 1 h. Then, The CNT matrix electrodes treated with TNB were heated at 673 K for 1 h. Finally, Electrode C was obtained.

### 2.3. Characteristics and investigations of the samples

The Brunauer-Emett-Teller (BET) surface area of the CNT/TiO<sub>2</sub> composites was evaluated from N<sub>2</sub> adsorption isotherm at 77 K using a BEL Sorp Analyzer (BEL, Japan). XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature with a diffractometer Shimata XD-D1 (Japan) using Cu K $\alpha$  radiation. SEM was carried out to observe the surface state and porous structure of the CNT/TiO<sub>2</sub> composites using a JSM-5200 JOEL electron microscope (Japan). EDX was used to measure the elemental analysis of the CNT/TiO<sub>2</sub> composites. UV-VIS spectra for the MB solution obtained from degradation by CNT/TiO<sub>2</sub> composites dispersion under different conditions were recorded using a Genspec (Hitachi, Japan) spectrometer.

### 2.4. PEC decompositions

The PEC decomposition was performed by using CNT/TiO<sub>2</sub> electrode and an aqueous solution of MB in a 100 mL glass container, and then irradiating the system with 20 W UV light at 365 nm, which was used at the distance of 100 mm from the solution in darkness box. The counter electrode was artificial graphite (TCK, Korea), which dimension was 9.95 mm  $\times$  39.5 mm  $\times$  5.95 mm. The same CNT/TiO<sub>2</sub> electrode was placed in 50 mL of 1.0  $\times$  10<sup>-5</sup> mol/L MB solution. The PEC degradation of MB was performed with a different potential voltage and UV light. The PEC activities of the CNT/TiO<sub>2</sub> electrodes were investigated using the PEC rate of MB, which was measured for 10 min, 20 min, 30 min, 40 min, 50 min and 60 min. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. And then the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

Table 1  
Surface areas of CNT/TiO<sub>2</sub> composites and pristine CNT and TiO<sub>2</sub>

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)
Pristine CNTs	299.2
Pristine TiO <sub>2</sub>	8.3
Electrode A	135.1
Electrode B	228.5
Electrode C	208.2

## 3. Results and Discussion

### 3.1. Structure and morphology of CNT/ TiO<sub>2</sub> composites

The values of the BET surface areas of CNT/TiO<sub>2</sub> composites are shown in Table 1. From the results of Table 1, the BET surface areas of pristine TiO<sub>2</sub> and CNT were 8.3 and 299.2 m<sup>2</sup>/g, respectively, while the BET surface areas of the CNT/TiO<sub>2</sub> composites changed from 135.1 m<sup>2</sup>/g to 228.5 m<sup>2</sup>/g with the introducing of TiO<sub>2</sub> through different methods, which suggesting that some porosity was developed during the heat treatment. It was considered that there are two aspect reasons. On the one hand, this could be attributed to the partial blocking of micropores by the formation of TiO<sub>2</sub> on the CNT surfaces with the heat treatment. On the other hand, the BET surface area decreased due to the curing of the polymer resin with heat treatment, which blocked the micropores and formed some new macropores. The same phenomena can be well confirmed by the SEM morphology of CNT/TiO<sub>2</sub> composites. However, the BET surface areas of all composites were small, and all surface areas showed considerably more decrease than

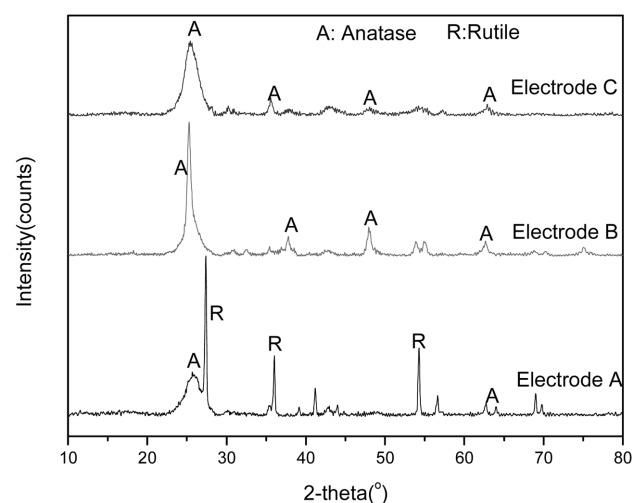


Fig. 2. XRD patterns of CNT/TiO<sub>2</sub> composites.

that of pristine CNTs, and an increased amount of CNTs would increase the surface area.

The XRD results for the catalyst samples are shown in Fig. 2. For Electrode A, the structure for the CNT/TiO<sub>2</sub> composites showed a mixture of anatase and rutile crystals. The samples were heated at 673 K for 1 h. The peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions maxima of (101), (004), (200) and (204) planes of anatase, indicating the CNT/TiO<sub>2</sub> composites developed existed in an anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks from (110),

(101), (111) and (211) of rutile. Therefore, it can be concluded that the CNT/TiO<sub>2</sub> composites developed had a mixture of structures of anatase and rutile crystals. In contrast to previous study [21], we have evidence that C/TiO<sub>2</sub> composites had a mixed structure of anatase and rutile crystals by crystallization when the temperature reached 973 K. In the present case, however, the crystals transformed from anatase to rutile at 673 K. The structures for the Electrode B and C show a typical single and clear anatase crystal structure. It is well known that the crystal structure of the titanium dioxide is

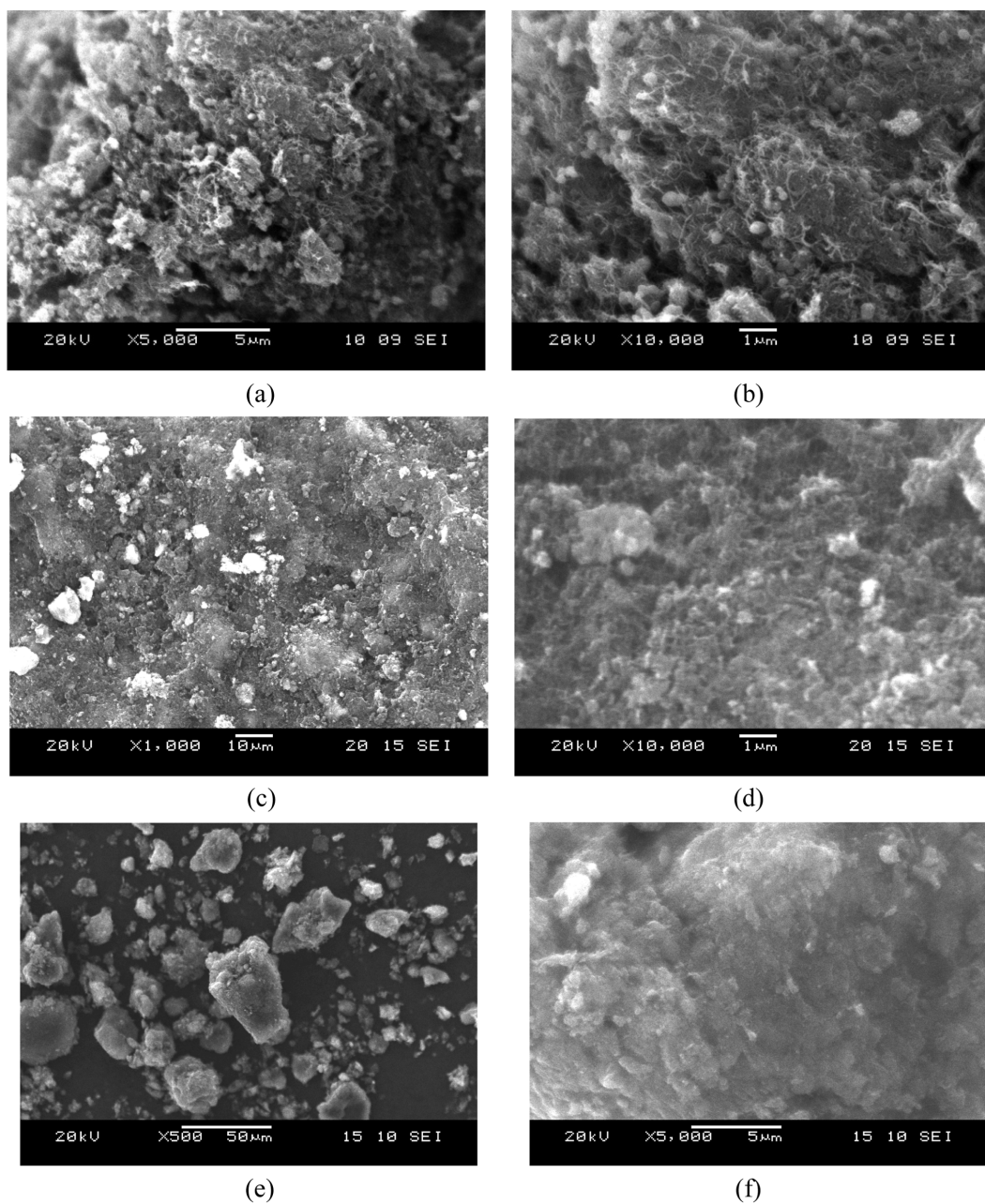
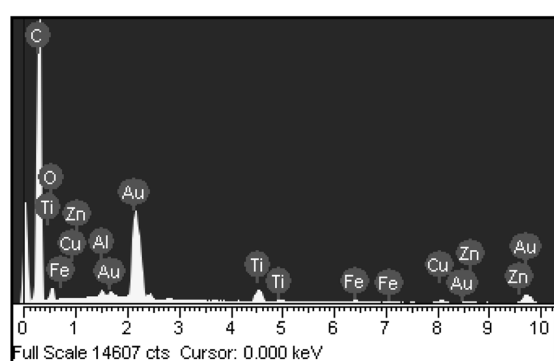


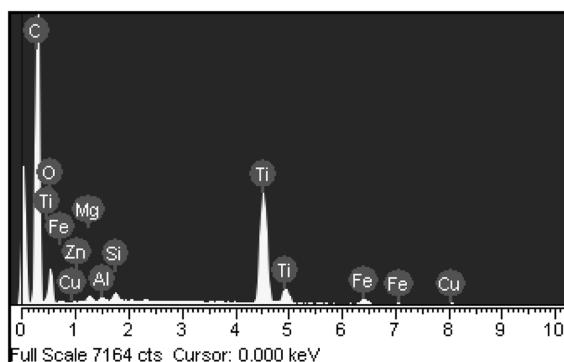
Fig. 3. SEM images obtained from powdered CNT/TiO<sub>2</sub> composites. (a): Electrode A (over-all scale), (b): Electrode A (close-up), (c): Electrode B (over-all scale), (d): Electrode B (close-up), (e): Electrode C (over-all scale), and (f): Electrode C (close-up).

mainly determined by the heat treated temperature. The samples were heated at 973 K for 1 h. The peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200) and (204) planes of anatase (JCPDS PD File No. 21-1272), indicating the developed CNT/TiO<sub>2</sub> composites existed in anatase state. As we know, the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973~1173 K [22]. The result is in accordance with the literature [23], so the results of XRD in this paper are reasonable.

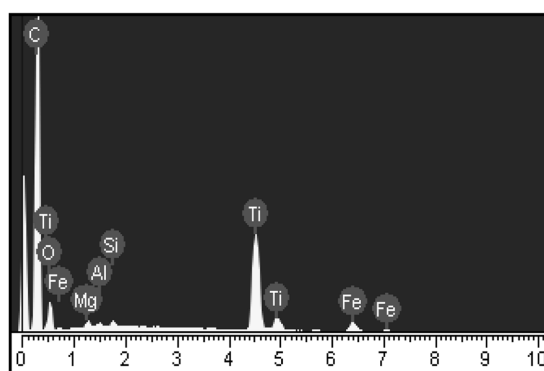
Fig. 3 shows the SEM morphology of CNT/TiO<sub>2</sub>



(a)



(b)



(c)

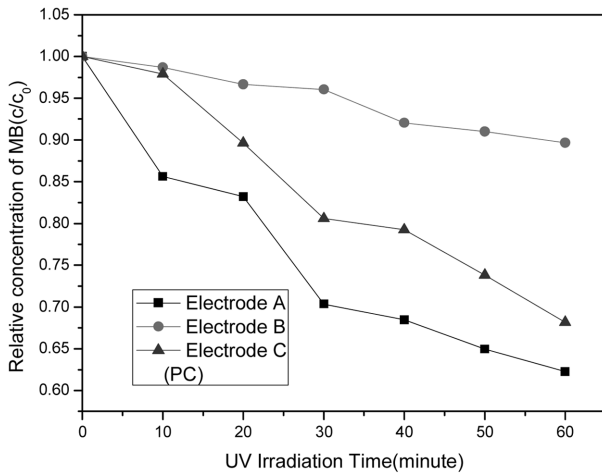
Fig. 4. EDX elemental microanalysis of CNT/TiO<sub>2</sub> composites. (a): Electrode A, (b): Electrode B, (c): Electrode C.

composites. Fig. 3 shows that TiO<sub>2</sub> particles were mixed well with the CNT network, in which the conductive network of CNTs would facilitate the electron transfer between the adsorbed MB molecules and the catalyst substrate. According to the Fig. 3(b), the image presents a close-up scale view of TiO<sub>2</sub> introduced from composites with external diameters ranging from 0.5 to 1.0  $\mu\text{m}$ . It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. This would be beneficial for the PEC reaction because the PEC reaction is carried out on the surfaces of the CNT/TiO<sub>2</sub> composites catalysts and the CNTs network. So the CNT/TiO<sub>2</sub> composites should show excellent PEC activity, although the dispersion of the TiO<sub>2</sub> particles for all CNT/TiO<sub>2</sub> composites prepared with different methods was not evidently changed among the CNTs networks. At the same time, the conductive of CNTs network can facilitate the electron transfer between the adsorbed MB molecules and the catalyst substrate [24-26]; it was beneficial for the PEC reaction because the PEC reaction is carried out on the surface of the CNT/TiO<sub>2</sub> composites catalysts and the CNTs network. So the CNT/TiO<sub>2</sub> composite would show an excellent PEC activity.

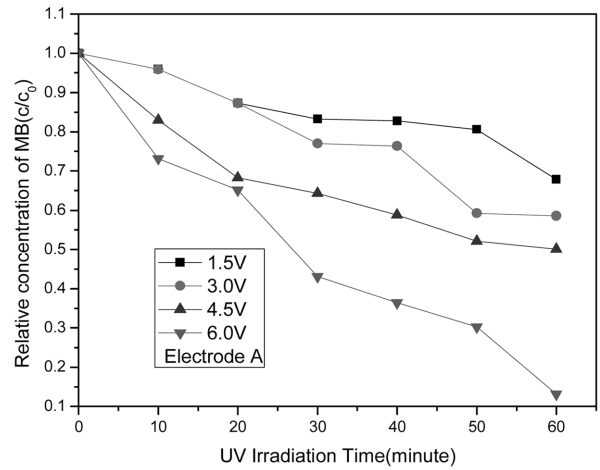
Fig. 4 shows the EDX spectra of CNT/TiO<sub>2</sub> composites prepared. From the EDX spectra, the main elements such as C, O and Ti were existed and other impure elements were also existed. The Ti content percents of Electrode A, B and C are 5.7 %, 14.9 % and 14.1 %, respectively; for Electrode A, the C element contents are highest in the three kinds of composites, while the Ti element contents are lowest.

### 3.2. PEC activities analysis

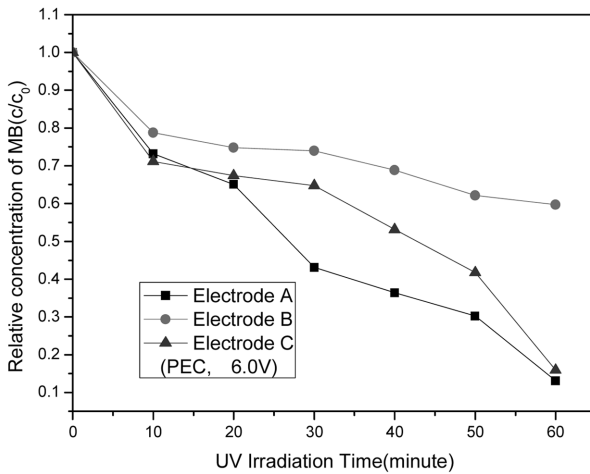
Fig. 5 shows the changes in relative concentration ( $c/c_0$ ) using CNT/TiO<sub>2</sub> composite electrodes in MB concentration of  $1 \times 10^{-5}$  mol/L under UV irradiation with or without electron current in the aqueous solution. From the present results in Fig. 5(a), it can be seen that the PC process of MB with fast degradation efficiency of Electrode A was observed. As the result of EDX, the Electrode A has the lowest content of Ti and the highest content of C. It is considered that decrease of MB concentration in the aqueous solution can be occurred in two physical phenomena such as PC decomposition by TiO<sub>2</sub> and adsorption by CNTs, and that the later was mainly here. From the Fig. 5(b), the PEC oxidation using Electrode A is higher than that of Electrode B and C. It was possible that the PEC oxidation increased with



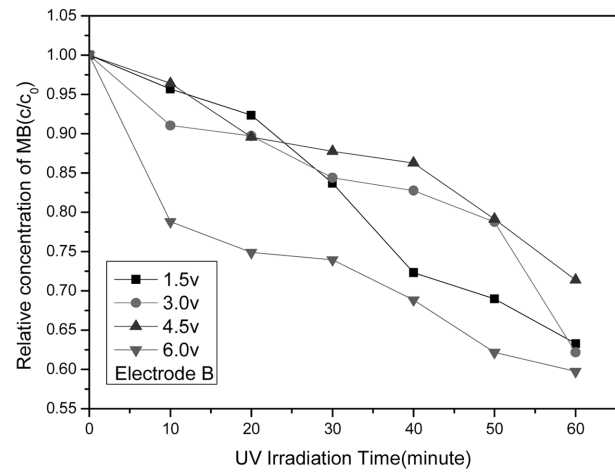
(a)



(a)



(b)

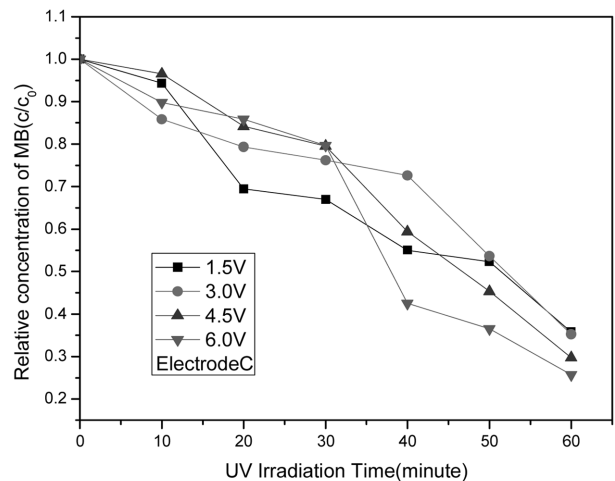


(b)

Fig. 5. Dependence of relative concentration ( $c/c_0$ ) of MB solution on time of UV irradiation for different CNT/TiO<sub>2</sub> electrodes: (a) PC (UV irradiation using the electrodes but without any electron current) and (b) PEC (UV irradiation using the electrodes with an electron current).

an increase of CNTs composition. The carbon content of Electrode A is the highest among the three samples, so the CNTs electro-assisted effect of Electrode A is better than that of Electrode B and C. In the comparison of the Fig. 5(a) and (b), it can be seen that the relative concentration ( $c/c_0$ ) of MB solution for all electrodes are higher by PC effect of CNT/TiO<sub>2</sub> electrode than that of PEC effect. It can be evidently indicated that two types of degradation of MB were electro-assistant activity of CNTs and PC performance of TiO<sub>2</sub>. So the efficiency of PEC oxidation for MB is higher than that of PC oxidation. According to the literatures [12, 13], it was possible that catalytic decomposition of MB solution could be attributed to combination effects between electro-assistant activity of CNTs and PC performance of TiO<sub>2</sub>.

Fig. 6 shows the dependence of relative concentration



(c)

Fig. 6. Dependence of relative concentration ( $c/c_0$ ) of MB in the aqueous solution on time of UV irradiation and different voltage using different CNT/TiO<sub>2</sub> composite electrodes. (a): Electrode A, (b): Electrode B, (c): Electrode C.

( $c/c_0$ ) of MB in the aqueous solution on time of UV irradiation and different voltage. As shown in Fig. 6(a),

for the Electrode A, the presence of a positive potential resulted in a significant upward trend in MB degradation. The PEC degradation of MB solution increased with an increase of the potential applied from 1.5 to 6.0 V at the same irradiation time. When the potential was increased to 6.0 V, a clear enhancement of the MB degradation in the experiments with CNT/TiO<sub>2</sub> composite electrode was observed. This suggests that the CNT networks have facilitated the separation of the photo-generated e/h<sup>+</sup> pairs in the composite under these levels of potential. The similar phenomena were observed in the cases of Electrode B and C, although the upward trends of increase were not identical. Compared with the three kinds of electrodes, at 60 minutes, the PEC degradation effects of MB solution using the Electrode C were greatest at the different applied potential.

It is well known that the electrons from the photon-induced electron-hole separation process must also be removed from the TiO<sub>2</sub> phase, in the absence of potential; this removal can be achieved via an oxidant, e.g. adsorbed oxygen molecules from the solution. In the CNT/TiO<sub>2</sub> composite electrodes, electrons are transferred from the TiO<sub>2</sub> phase (low electron conductivity) into the carbon phase (high electron conductivity). This process must overcome the interfacial resistance, which is largely fixed by the properties of the two solid phases. Therefore, to enable electron transfer, a sufficient or higher anodic potential is needed, which explains partly the photo-currents being relatively small at low anodic potentials, but significantly larger at higher polarisations. Furthermore, the TiO<sub>2</sub> particles mixed well with the CNT networks, which allows a local potential difference across the TiO<sub>2</sub> phase to be developed throughout the sample, resulting in more effective e/h<sup>+</sup> separation within the entire sample.

In our case, as the applied potential in PEC process, the recombination of photogenerated e/h<sup>+</sup> pairs was suppressed by the externally applied electric field, and thus the life of the e/h<sup>+</sup> got longer, and hence are able to migrate to the solid-liquid interface, promoting redox reactions [27, 28]. Based on the experimental findings and the analysis above, this PEC degradation analysis can fit well to the results of MB PEC degradation using the prepared CNT/TiO<sub>2</sub> composite electrodes, which showed an increase trend when the potential was increased.

#### 4. Conclusion

In this study, we presented the fabrication and charac-

terization of CNT/TiO<sub>2</sub> composites electrodes. The BET surface areas decreased for CNT/TiO<sub>2</sub> composites prepared with different methods. XRD data revealed that the structure for the Electrode A showed a mixing anatase and rutile crystals. However, the prepared Electrode B and C showed a typical single and clear anatase crystal structure. The SEM microphotographs of CNT/TiO<sub>2</sub> composites showed that TiO<sub>2</sub> particles were fixed on the surface of the CNTs network in the forms of small clusters. From the EDX data, the main elements such as C, O and Ti were existed. The results demonstrated that the PEC oxidation of MB solution can be contributed to the combination effects of PC decomposition by TiO<sub>2</sub>, electro-assisted of CNTs network and the function of applied potential. In comparison of PC oxidation and PEC oxidation, the efficiency of PEC oxidation for MB is higher than that of PC oxidation. There was a clear enhancement trend of the MB degradation using the prepared CNT/TiO<sub>2</sub> composite electrodes with an increase of applied potential.

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